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HEAT-DEVELOPABLE PHOTSENSITIVE MATERIAL

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References cited:

Japanese Kokai Patent Application
No. Sho 54[1979]-51820 (JP, A)

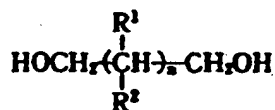
Japanese Kokai Patent Application
No. Sho 58[1983]-107534 (JP, A)

[There are no amendments to this patent.]

Claim

A heat-developable photosensitive material characterized by having a photosensitive constituent layer containing an organic silver salt (a), a photosensitive silver salt (b), a reducing agent (c), and a binder (d) on a substrate, said photosensitive silver salt (b) being a chemically sensitized silver halide, and the aforementioned photosensitive constituent layer containing a compound (e) represented by the following general formula (I).

General formula (I)



(where R¹ and R² can be the same or different and represent a hydrogen atom, hydroxymethyl group, or hydroxyethyl group; n is an integer in the range of 0-7.)

Detailed explanation of the invention

The present invention pertains to a heat-developable photosensitive material. In particular, the present invention pertains to a heat-developable photosensitive material with an excellent developing property.

The well-known photographic method using photosensitive silver halide is superior to other photographic methods in photosensitivity, gradation, image storability, etc. It has become the most widely used photographic method.

In this method, however, since a wet processing method is used for development, fixing, rinsing, and other processing steps, the entire process takes a long time and a lot of work. Also, the processing chemicals are harmful to the human body, and the processing room or the operator might be contaminated by the aforementioned chemicals. Another problem is the pollution caused by the waste liquid. Consequently, it is desired to develop a photosensitive material which uses a photosensitive silver halide and can be processed in a dry manner.

Various dry processing photographic methods have been proposed. Among them, the method in which a heat-developable photosensitive material is used which can be developed by performing a heat treatment has attracted much attention because the photosensitive material meets the aforementioned demands. Examples of such a heat-developable photosensitive material are described in Japanese Kokoku Patent Nos. Sho 43[1968]-4921, Sho 43[1968]-4924, etc. The photosensitive material consists of an organic silver salt, a silver halide, and a reducing agent.

According to this technology, a latent image is first formed by irradiating light on a photosensitive silver salt, such as a silver halide. Then, with the latent silver image used as the catalyst nucleus, a silver image is obtained by carrying out an oxidation-reduction reaction using an organic silver salt and a reducing agent during heating. As described in Japanese Kokoku Patent Nos. Sho 43[1968]-4921, Sho 43[1968]-4924, Sho 44[1969]-26582, Sho 45[1970]-18416, Sho 45[1970]-12700, Sho 45[1970]-22185, Japanese Kokai Patent Application Nos. Sho 49[1974]-52626, Sho 52[1977]-31728, Sho 52[1977]-137321, Sho 52[1977]-141222, Sho 52[1977]-137321 [sic; repeated], Sho 52[1977]-141222 [sic; repeated], Sho 53[1978]-36224, Sho 53[1978]-37610, and US Patent No. 3330633, No. 3794496, No. 4105451, No. 4123274, No. 4168980, etc., examples of the organic silver salts that can be used for the aforementioned heat-developable photosensitive material include silver salts of aliphatic carboxylic acids, such as silver laurate, silver myristate, silver palmitate, silver stearate, silver arachidonate, silver behenate, silver α -(1-phenyltetraazothio)acetate, etc.

These silver salts are used together with color tone agents. However, as a photographic characteristic, the problem of thermal fog becomes serious. Also, harmful mercuric salts are mainly used in practical application as a thermal fog inhibitor.

In order to increase the sensitivity of the photosensitive material, it is preferred to prepare the silver halide in a hydrophilic binder. It is particularly preferred to prepare the silver halide in a gelatin derivative. As far as the coating property is concerned, it is also desired to use a gelatin derivative during simultaneous laminate coating because it coagulates (due to the setting property) under cooling. Consequently, it is preferred to use a hydrophilic binder as the binder of the photosensitive material. A gelatin derivative is particularly preferred.

However, the aforementioned silver salts of aliphatic carboxylic acids are very difficult to disperse in the hydrophilic binder, and the dispersion stability is also poor.

In addition to the aforementioned examples of silver salts, as described in Japanese Kokoku Patent Nos. Sho 44[1969]-26582, Sho 45[1970]-12700, Sho 45[1970]-18416, Sho 45[1970]-22185, Japanese Kokai Patent Application Nos. Sho 52[1977]-31728, Sho 52[1977]-137321, etc., other silver salts that can be used include silver salts of imino groups, such as benzotriazole silver salt, 5-nitrobenzotriazole silver salt, 5-chlorobenzotriazole

silver salt, 5-methoxybenzotriazole silver salt, imidazole silver salt, pyrazole silver salt, urazole silver salt, 1,2,4-triazole silver salt, IH-tetraazole silver salt, etc.

Such silver salt is contained in a binder together with a reducing agent. After a latent image is formed, heat development is performed to obtain an image. However, when a gelatin binder is used, good dispersion and dispersion stability can be achieved. Nevertheless, the highest density of the obtained image lessens. In some cases, no image can be obtained at all.

Japanese Kokoku Patent No. Sho 45[1970]-12700 disclosed a heat-developable photosensitive material containing an organic carboxylic acid and at least one of the aforementioned salts. However, the improvement in the developing property obtained by using this material is insufficient.

The melt forming compounds, such as 1,3-dimethylurea, disclosed in US Patent No. 3438776 and No. 3667959 show some effects but also are not sufficient. Therefore, it is desired to develop an excellent development accelerating technology.

A purpose of the present invention is to provide a heat-developable photosensitive material which does not need harmful thermal fog inhibitors, especially mercuric salts.

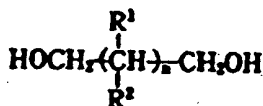
Another purpose of the present invention is to provide a heat-developable photosensitive material which has a good developing property and can realize high density when a silver salt is used which is easy to disperse in a hydrophilic binder, especially in a gelatin derivative, and has a good dispersion stability.

Yet another purpose of the present invention is to provide a heat-developable photosensitive material containing a melt forming compound which does not deteriorate the storability like in conventional melt forming compounds, such as 3-dimethylurea, when using a chemically sensitized halide.

Other purposes can be determined from the description of the specification.

In order to realize the aforementioned purposes, the present invention provides a heat-developable photosensitive material characterized by having a photosensitive constituent layer containing an organic silver salt (a), a photosensitive silver salt (b), a reducing agent (c), and a binder (d) on a substrate, said photosensitive silver salt (b) being a chemically sensitized silver halide and the aforementioned photosensitive constituent layer containing a compound (e) represented by the following general formula (I). Said components (a)-(e) can exist in any part of the photosensitive material as a result of diffusion, penetration, etc. during the manufacturing process or storage.

General formula (I)



where R^1 and R^2 can be the same or different and represent a hydrogen atom, hydroxymethyl group, or hydroxyethyl group; n is an integer in the range of 0-7.

By using the compound represented by said formula (I) as an additive, the heat-developable photosensitive material of the present invention is provided with improved developing property, and a highest density can be obtained to a high degree and at a high sensitivity. Also, dispersion in a gelatin aqueous solution becomes easy, and the dispersion stability is improved. The good developing property can be obtained even in a gelatin binder. In addition, there is no need to use a mercuric salt to prevent thermal fog.

In the following, this invention will be explained in more detail.

As described in Japanese Patent Application No. 57[1982]-82064, the present inventors found that the compound represented by said formula [I] has an excellent development improving effect. It was also found that these compounds are particularly effective when a chemically sensitized silver halide is used as the photosensitive silver salt. The melt forming compounds, such as 1,3-dimethylurea, described in US Patent No. 3438776 and No. 3667959 will significantly deteriorate the storability of the heat-developable photosensitive material when a chemically sensitized silver halide is used as the photosensitive silver salt. However, the present inventors found that the compounds described in said Japanese Patent Application No. Sho 57[1982]-82064 can significantly improve development without deteriorating storability.

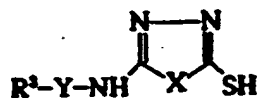
First, the compound represented by general formula [I] used in the present invention will be explained. Specific examples of the compounds represented by said general formula [I] include ethylene glycol, glycerin, 1,2,3,4-butanetetrol, 1,2,3,4,5-pentanepentol, pentaerythritol, 1,2,3,4,5,6-hexanehexol, 1,2,3,4,5,6,7-heptaneheptol, 1,2,3,4,5,6,7,8-octaneoctol, 1,2,3,4,5,6,7,8,9-nonanenonol, etc.

The use amount of the compound represented by said general formula [I] varies depending on the type of organic silver salt used, type of reducing agent used, and types of other additives. However, the use amount is preferably in the range of 0.1-5 g, more preferably in the range of 0.3-2 g with respect to 1 g of the binder.

It is preferred to use the compounds represented by general formulas [II] and [III] shown below as other additives in the present invention.

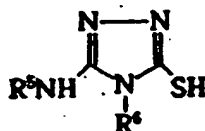
When these compounds are used together with the compound represented by general formula [I] in the present invention, the development accelerating effect can be significantly improved when a hydrophilic compound, such as a gelatin or gelatin derivative, is used.

General formula [II]



where R³ represents a hydrogen atom, hydroxy group or alkyl group with/without a substituent, alkenyl group, aryl group, or alkoxy group; Y represents a sulfonyl group or carbonyl group; X represents a sulfur atom or =N-R⁴; R⁴ represents a hydrogen atom, amino group or alkyl group with/without a substituent, aryl group, or alkenyl group.

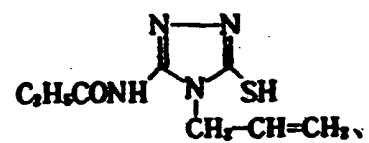
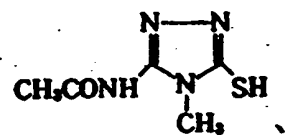
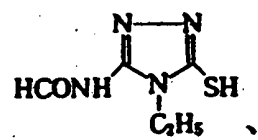
General formula [III]

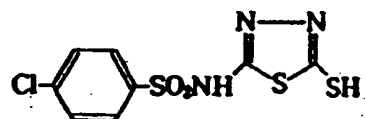
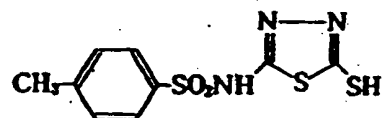
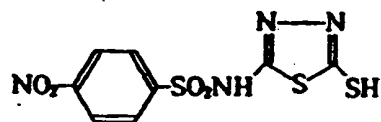
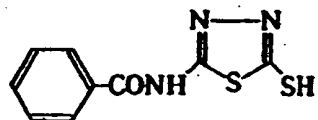
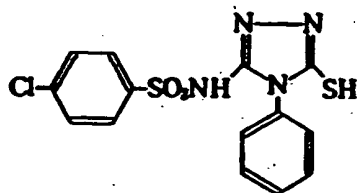
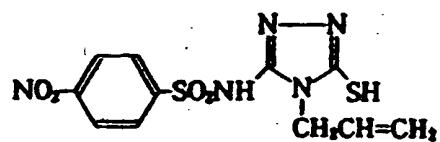


where R⁵ represents a hydrogen atom, amino group or alkyl group with/without substituent, alkenyl group, or aryl group; R⁶ represents a hydrogen atom, amino group, alkyl group, alkenyl group, or aryl group.

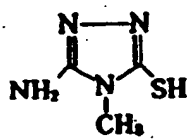
Specific examples of the aforementioned two compounds are listed below.

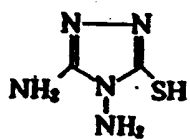
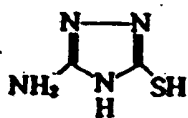
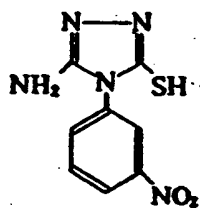
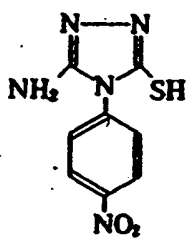
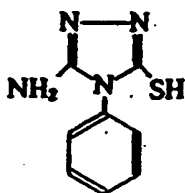
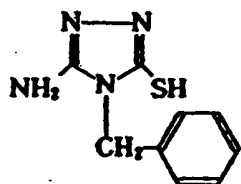
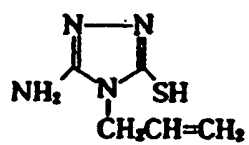
Specific examples of the compounds represented by general formula [II] include the following:

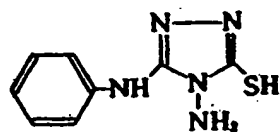
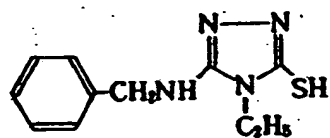
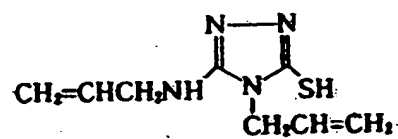
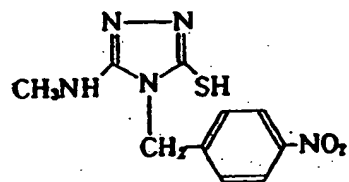
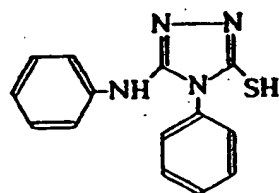
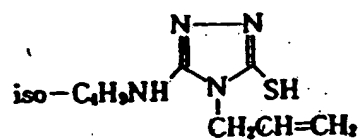
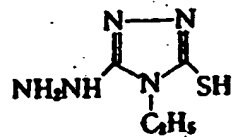
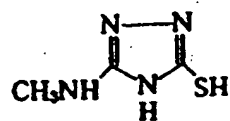




Specific examples of the compounds represented by general formula [III] include the following:







The contents of these compounds are preferably in the range of 0.001-10 mol, or more preferably in the range of 0.005-0.5 mol with respect to 1 mol of the organic silver salt.

Also, it is preferred to use the compounds disclosed in Japanese Kokai Patent Application No. Sho 52[1977]-33722 (US Patent No. 3994732 and No. 4123282) and Japanese Patent Application No. Sho 56[1981]-93396, such as phthalic acid, maleic acid, methylenesuccinic acid, quinolinic acid, and phthalazine, as additives used for improving characteristics.

Examples of the organic silver salts that can be used in the present invention include silver salts of aliphatic carboxylic acids, such as silver laurate, silver myristate, silver palmitate, silver stearate, silver arachidonate, silver behenate, and silver α -(1-phenyltetraazothio)acetate, and silver salts of aromatic carboxylic acids, such as silver benzoate and silver phthalate, as described in Japanese Kokoku Patent Nos. 43[1968]-4921, Sho 44[1969]-26582, Sho 45[1970]-18416, Sho 45[1970]-12700, Sho 45[1970]-22185, Japanese Kokai Patent Application Nos. Sho 49[1974]-52626, Sho 52[1977]-31728, Sho 52[1977]-137321, Sho 52[1977]-141222, Sho 53[1978]-36224, Sho 53[1978]-37610, and US Patent No. 3330633, No. 3794496, No. 4105451, No. 4123274, No. 4168980, etc., silver salts of imino groups, such as the silver salts of benzotriazole, 5-nitrobenzotriazole, 5-chlorobenzotriazole, 5-methoxybenzotriazole, 4-sulfobenzotriazole, 4-hydroxybenzotriazole, 5-aminobenzotriazole, 5-carboxybenzotriazole, imidazole, benzimidazole, 6-nitrobenzimidazole, pyrazole, urazole, 1,2,4-triazole, 1H-tetrazole, saccharin, phthalazinone, and phthalimide, as described in Japanese Kokoku Patent No. Sho 44[1969]-26582, 45[1970]-12700, Sho 45[1970]-18416, Sho 45[1970]-22185, Japanese Kokai Patent Application Nos. Sho 52[1977]-31728, and Sho 52[1977]-137321, as well as 2-mercaptobenzoxazole, mercaptooxazole, 2-mercaptobenzothiazole, 2-mercaptobenzoimidazole, 3-mercapto-4-phenyl-1,2,4-triazole, 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene, and 5-methyl-7-hydroxy-1,2,3,4,6-pentaazaindene.

Among the aforementioned organic silver salts, it is preferred to use the silver salts of imino groups in the present invention. The silver salts of benzotriazole derivatives are particularly preferred.

The photosensitive silver salt used in the present invention is a photosensitive silver halide. Examples include silver chloride, silver bromide, silver iodide, silver chlorobromide, silver chlorobromiodide, silver chloriodide, and silver iodobromide. These silver halides can be prepared using any well-known method in the technical field of photography, such as single jet method or double jet method. The silver halide can be used in the form of either coarse particles or fine particles, with a particle size in the range of 1.5-0.001 μm , or preferably in the range of about 0.5-0.05 μm .

The photosensitive halide silver which is prepared as described above can be added and used as the photosensitive silver salt in the present invention.

According to another preparation method, a component for forming the photosensitive silver salt can be used together with the aforementioned organic silver salt to form a photosensitive silver halide as part of the organic silver salt. Examples of the developing silver salt forming component that can be used in this preparing method include inorganic halides, such as halides represented by MX_n (where M represents H, NH_4 , or a metal atom; X represents Cl, Br, or I; n is 1 when M represents H or NH_4 and is the valence when M is a metal atom; examples of the metal atoms include lithium, sodium, potassium, rubidium, cesium, copper, gold, beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, mercury, aluminum, indium, lanthanum, ruthenium, thallium, germanium, tin, lead, antimony, bismuth, chromium, molybdenum, tungsten, manganese, rhenium, iron, cobalt, nickel, rhodium, palladium, osmium, iridium, platinum, cerium, etc.); halogen-containing metal complex (such as K_2PtCl_6 , K_2PtBr_6 , $HAuCl_4$, $(NH_4)_2IrCl_6$, $(NH_4)_3IrCl_6$, $(NH_4)_2RuCl_6$, $(NH_4)_3RuCl_6$, $(NH_4)_3RhCl_6$, and $(NH_4)_3RhBr_6$), onium halides (such as tetramethylammonium bromide, trimethylphenylammonium bromide, cetylthyltrimethylammonium bromide, 3-methylthiazolium bromide, trimethylbenzylammonium bromide, and other quaternary ammonium halides, tetraethylphosphonium bromide and other quaternary phosphonium halides, benzylethylmethyl bromide, 1-ethylthiazolium bromide, and other tertiary sulfonium halides), halogenated hydrocarbons (such as iodoform, bromoform, carbon tetrabromide, 2-bromo-2-methylpropane, etc.), N-halogen compounds (such as N-chlorosuccinimide, N-bromosuccinimide, N-bromophthalimide, N-bromoacetamide, N-iodosuccinimide, N-bromophthalazinone, N-chlorophthalazinone, N-bromoacetanilide, N,N-dibromobenzenesulfonamide, N-bromo-N-methylbenzenesulfonamide, 1,3-dibromo-4,4-dimethylhydantoin, etc.), as well as other halogen-containing compounds (such as triphenylmethyl chloride, triphenylmethyl bromide, 2-bromobutyric acid, and 2-bromoethanol).

The silver halide used for the heat-developable photosensitive material of the present invention is chemically sensitized according to the well-known method in the corresponding field. Examples of the effective sensitizers that can be used include active gelatin, sulfur sensitizers (such as sodium thiosulfate, allyl thiocarbamide thiourea, allyl isothiocyanate, etc.), selenium sensitizers (such as N,N-dimethylselenourea, selenourea, etc.), reducing sensitizers (such as triethylenetetramine, stannic chloride, etc.), and various types of metal sensitizers, such as potassium chloroaurate, potassium aurithiocyanate, potassium chloroaurate, 2-aurosulfobenzothiazole methyl chloride, ammonium chloropaladate, potassium chloroplatinate, sodium chloropaladate, etc. These sensitizers can be used either alone or as a mixture of several types. When a metal sensitizer is used, ammonium rhodanate can be used as an aide. Also,

examples of the silver halide emulsions that can be used in the present invention for stabilization include those disclosed in US Patent No. 2444607, No. 2716062, No. 3512982, No. 3726686, No. 3717465, No. 3342596, German Patent Application No. 1189380, UK Patent No. 1363921, Japanese Kokoku Patent Nos. Sho 43[1968]-4133, Sho 47[1972]-4417, Sho 39[1964]-2825, and Sho 49[1974]-13566. Preferred examples include

5,6-trimethylene-7-hydroxy-s-triazolo[1,5-a]pyrimidine,
 5,6-tetramethylene-7-hydroxy-s-triazolo[1,5-a]pyrimidine,
 5-methyl-7-hydroxy-s-triazolo[1,5-a]pyrimidine, 7-hydroxy-s-triazolo[1,5-a]pyrimidine,
 5-methyl-6-bromo-7-hydroxy-s-triazolo[1,5-a]pyrimidine, gallic esters (such as isoamyl gallate, dodecyl gallate, propyl gallate, and sodium gallate), mercaptans (such as 1-phenyl-5-mercaptotetrazole and 2-mercaptobenzothiazole), benzotriazoles (such as benzotriazole, 5-bromobenzotriazole, and 4-methylbenzotriazole), etc.

Other silver halide emulsions that can be used in the present invention include the sulfur-containing amino acid compounds disclosed in UK Patent No. 1343904 or other latent stabilizers as well as the cadmium salts and rhodium salts disclosed in UK Patent No. 775197 and No. 3488709 or other gradation adjusting agents.

The photosensitive silver salts and the photosensitive silver salt forming components can be used in combination in various methods. The content is in the range of 0.001-10 mol, or preferably in the range of 0.01-3 mol with respect to 1 mol of the organic silver salt.

Examples of the reducing agents that can be used in the present invention include phenols (such as p-phenylphenol, p-methoxyphenol, 2,6-di-tert-butyl-p-cresol, N-methyl-p-aminophenol, etc.), sulfonamide phenols (such as 4-benzenesulfonamide phenol, 2-benzenesulfonamide phenol, 2,6-dichloro-4-benzenesulfonamide phenol, 2,6-dibromo-4-(p-toluenesulfonamide phenol, etc.), polyhydroxybenzenes (such as hydroquinone, tert-butylhydroquinone, 2,6-diethylhydroquinone, chlorohydroquinone, carboxyhydroquinone, catechol, 3-carboxycatechol, etc.), naphthols (such as α -naphthol, β -naphthol, 4-aminonaphthol, 4-methoxynaphthol, etc.), hydroxybinaphthyls and methylenebisnaphthols (such as 1,1'-dihydroxy-2,2'-bisnaphthyl, 6,6'-dibromo-2,2'-dihydroxy-1,1'-bisnaphthyl, 6,6'-dinitro-2,2'-dihydroxy-1,1'-bisnaphthyl, 4,4'-dimethoxy-1,1'-dihydroxy-2,2'-bisnaphthyl, bis(2-hydroxy-1-naphthyl)methane, etc.), methylenebisphenols (such as 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane, 1,1-bis(2-hydroxy-3-tert-butyl-5-methylphenyl)methane, 1,1-bis(2-hydroxy-3,5-di-tert-butylphenyl)methane, 2,6-methylenebis(2-hydroxy-3-tert-butyl-5-methylphenyl)-4-methylphenol, α -phenyl- α , α -bis(2-hydroxy-3,5-di-tert-butylphenyl)methane, α -phenyl- α , α -bis(2-hydroxy-3-tert-butyl-5-methylphenyl)methane,

1,1-bis(2-hydroxy-3,5-dimethylphenyl)-2-methylpropane,
 1,1,5,5-tetrakis(2-hydroxy-3,5-dimethylphenyl)2,4-ethylpentane,
 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane,
 2,2-bis(4-hydroxy-3-methyl-5-tert-butylphenyl)propane,
 2,2-bis(4-hydroxy-3,5-di-tert-butylphenyl)propane, etc.), ascorbic acids, 3-pyrazolidones,
 pyrazolidones, pyrazolines, pyrazolones, hydrazones, and p-phenylenediamines.

When hydrazone or p-phenylenediamine is used as the reducing agent, phenol-based compounds, naphthol-based compounds, pyrazolone, pyrazolotriazole, indazole, pyrazolobenzimidazole, pyrazoline, or other compounds with active methylene disclosed in US Patent No. 3531286, No. 3764328, and Japanese Kokai Patent Application No. Sho 56[1981]-27132 can be used together to obtain color images.

These reducing agents can be used either alone or as a mixture of several types. The amount of reducing agent used varies depending on the type of organic silver salt used, the type of photosensitive silver salt used, and the types of other additives. However, the amount of reducing agent is usually in the range of 0.05-10 mol, or preferably in the range of 0.1-3 mol with respect to 1 mol of organic silver salt.

Examples of the binders that can be used for the heat-developable photosensitive material of the present invention include polyvinylbutyral, polyvinyl acetate, ethylcellulose, polymethyl methacrylate, cellulose acetate butyrate, polyvinyl alcohol, gelatin, phthalated gelatin and other gelatin derivatives, as well as other synthetic or natural polymeric substances.

It is preferred to use a gelatin derivative among the aforementioned binders in the present invention. Gelatin is particularly preferred.

The amount of binder used is usually in the range of 0.5-10 g, or preferably in the range of 1-5 g with respect to 1 g of the silver salt.

In addition to the aforementioned components, if necessary, spectral sensitizing dyes, halation preventing dyes, print-out inhibitors, non-mercury type fog inhibitors, and other well-known additives can be added to the heat-developable photosensitive material of the present invention.

Spectral sensitizing dyes that are effective on the silver halide emulsion can be used. Examples include cyanine, merocyanine, rhodacyanine, styryl coloring materials, etc.

Examples of the print-out inhibitors include tetrabromobutane, tribromoethanol, 2-bromo-2-triacetamide, 2-bromo-2-trisulfonylacetamide, 2-tribromomethylsulfonylbenzothiazole, 2,4-bis(tribromomethyl)-6-methyltriazine, etc.

The heat-developable photosensitive material of the present invention may also contain a water-releasing agent, that is, a compound which can release water under heating. Examples of the water-releasing agents include trisodium phosphate dodecahydrate, sodium sulfate

decahydrate, iron ammonium sulfate hexahydrate, ammonium alum tetracosahydrate, potassium alum tetracosahydrate, magnesium acetate tetrahydrate, manganese acetate tetrahydrate, or other compounds containing water of crystallization.

The heat-developable photosensitive material of the present invention may also contain a water-retaining compound in order to keep the water content in the photosensitive material at a constant level. Examples of the water-retaining compounds include the polyalkylene oxide (polyglycol), hydroxyethylcellulose, carboxymethylcellulose, etc. that are mentioned in the specification of US Patent No. 3347765

The constituent components listed above which display the functions of the heat-developable photosensitive material of the present invention in a primary or secondary manner are coated on a support and contained separately in multiple heat-developable constituent layers which display the functions of the heat-developable photosensitive material of the present invention in a primary or secondary manner corresponding to the characteristics, respectively. Of course, it is also possible to use a single heat-developable constituent layer which contains all of the constituent components listed above.

Examples of the support that can be used for the heat-developable photosensitive material of the present invention include polyethylene film, cellulose acetate film, polyethylene terephthalate film, or other synthetic plastic films, and photographic paper, printing paper, baryta paper, resin coated paper, or other paper supports. These supports may have a primer layer.

Together with a binder and an appropriate solvent, the aforementioned components (a)-(e) are coated as a heat-developable photosensitive constituent layer on a support. The coating thickness is in the range of 1-1000 μ , or preferably in the range of 3-20 μ after drying. If necessary, it is also possible to form an upper coating layer on the heat-developable photosensitive constituent layer.

The aforementioned support can also contain a part of each of components (a)-(e) used in the present invention as a result of penetration from the single or multiple heat-developable photosensitive constituent layers. The aforementioned upper coating layer and/or primer layer can also contain a part of each of said components (a)-(e) used in the present invention as a result of penetration from the heat-developable photosensitive constituent layer.

In the present invention, the heat-developable photosensitive constituent layer can be formed in multiple layers, including a constituent layer containing a silver salt as the main component and a constituent layer containing a reducing agent as the main component.

After the heat-developable photosensitive material prepared as described above is exposed directly as a photosensitive material, development can be performed simply by heating it to a temperature in the range of 80-200°C for 1-60 sec. If necessary, a water-impermeable

material can be adhered to the photosensitive material before development is performed. It is also possible to perform preheating at a temperature in the range of 70-180°C before exposure.

Examples of the light source that can be used for image exposure include a tungsten lamp, fluorescent lamp, mercury lamp, iodine lamp, xenon lamp, CRT light source, laser light source, etc.

In the following, this invention will be explained in more detail with reference to application examples. The present invention, however, is not limited to these application examples.

First, the preparation and compositions of the components used in the application examples will be explained below.

(Preparation of benzotriazole silver salt)

16.9 g of silver nitrate were dissolved in 200 mL of pure water. Separately, 12.0 g of benzotriazole were dissolved in 40 mL of methanol. The methanol solution of benzotriazole was added to the aqueous solution of silver nitrate under stirring at room temperature, followed by 30 min of stirring. The generated benzotriazole silver salt was filtered, washed with water and methanol, and then dried. 22.5 g of benzotriazole silver salt were obtained.

(Preparation of 4-sulfobenzotriazole silver ammonium salt)

16.9 g of silver nitrate were dissolved in 200 mL of pure water, followed by adding 35 mL of 29% ammonia water. Separately, 20.1 g of 4-sulfobenzotriazole were dissolved in 50 mL of pure water. The aqueous solution of 4-sulfobenzotriazole was added to the aqueous solution of silver nitrate ammonia solution under stirring at room temperature, followed by 30 min of stirring. The generated 4-sulfobenzotriazole silver ammonium salt was filtered, washed with water, and dried. 21.5 g of 4-sulfobenzotriazole silver ammonium salt were obtained.

(Preparation of 4-hydroxybenzotriazole silver salt)

16.9 g of silver nitrate were dissolved in 200 mL of pure water. Separately, 13.6 g of 4-hydroxybenzotriazole were dissolved in 40 mL of methanol. The methanol solution of 5 [sic, 4]-nitrobenzotriazole was added to the aqueous solution of silver nitrate under stirring at room temperature, followed by 30 min of stirring. The generated 4-hydroxybenzotriazole silver salt was filtered, washed with water and methanol, and dried. 24.0 g of 4-hydroxybenzotriazole silver salt were obtained.

(Preparation of benzotriazole silver salt)

11.3 g (0.05 mol) of benzotriazole silver salt were added to 300 mL of an 8% gelatin aqueous solution, followed by 24 h of dispersion performed in a ball mill. As a result, a homogeneous suspension of benzotriazole silver salt was obtained.

Application Example 1

0.2- μ m octahedronal silver iodobromide containing 2 mol% silver iodide was prepared using the controlled double jet method with the pAg maintained at 9.5. 50 mg of sodium sulfate and 15 mg of sodium chloroargentate were added with respect to 1 mol of silver halide to the aforementioned emulsion, followed by 50 min of chemical aging performed at 60°C.

A sample of the heat-developable photosensitive material was manufactured as follows. 30 mL of the aforementioned emulsion (containing 0.05 mol of silver and 4 g of gelatin) were added to 300 mL of each of the aforementioned benzotriazole silver salt suspensions. Then, 10 mL of a 10% alkanol B aqueous solution (alkylnaphthalenesulfonic acid soda, product of DuPont Co.) were added, followed by stirring to obtain a dispersion.

10 mL of 8% gelatin, 10mL of 50% alcohol and a developing solution containing 440 mg of ascorbic acid, 4 mg of 4-allyl-3-amino-5-mercapto-1,2,4-triazole, and the additives listed in Table 1 were added to 16.5 mL of the aforementioned dispersion, followed by stirring. The obtained mixed solution was coated on a piece of photographic baryta paper in such a way that the silver amount was 9 mg/100 cm². Then, the paper was dried, giving samples 1-8 of heat-developable photosensitive material.

Exposure was performed for each of the obtained samples of the heat-developable photosensitive material through an optical wedge.

The exposure density was 0.01 mJ/cm² in the maximum exposure part of sample 1.

Subsequently, each sample was brought into contact with a hot metal plate at 140°C for 15 sec to perform heat development. Also, each of the aforementioned samples was developed under the same conditions after it was stored at 40°C and 80% RH for 2 days.

Table 1 shows the results.

Table 1

No	添加剤 ⑨	添加量 g ⑩	⑫ 即 ⑬ 日 ⑪			40°C 80% 2日 ⑭			備考 ⑮
			比感度 ⑫	カブリ ⑬	D ₅₀ ⑭	比感度 ⑫	カブリ ⑬	D ₅₀ ⑭	
①	ブタンテトロール	1.0	100	0.14	1.20	82 ⑫	0.20 ⑬	1.05	本発明 ⑯
②	ペンタンペントール	#	105	0.15	1.40	85	0.25	1.10	
③	ペンタエリスリトール	#	95	0.10	1.22	89	0.19	1.00	
④	ヘキサンヘキソール	#	102	0.12	1.35	80	0.29	0.95	
⑤	アセトアミド	#	105	0.15	1.29	25	0.29	0.55	本発明外 ⑰
⑥	1,3-ジメチル尿素	#	102	0.12	1.35	20	0.30	0.60	

No	添加剤 ⑨	添加量 g ⑩	⑫ 即 ⑬ 日 ⑪			40°C 80% 2日 ⑭			備考 ⑮
			比感度 ⑫	カブリ ⑬	D ₅₀ ⑭	比感度 ⑫	カブリ ⑬	D ₅₀ ⑭	
⑦	マロン酸	#	82	0.15	0.51	— ⑫	0.35 ⑬	0.38	
⑧	ジグリコール酸	#	79	0.10	0.44	—	0.38	0.35	

- Key:
- 1 Butanetetrol
 - 2 Pentanepentol
 - 3 Pentaerythritol
 - 4 Hexanehexol
 - 5 Acetamide
 - 6 1,3-dimethylurea
 - 7 Malonic acid
 - 8 Diglycolate
 - 9 Additive
 - 10 Amount added, g
 - 11 The same day
 - 12 Specific sensitivity
 - 13 Fog
 - 14 40°C 80% RH 2 days
 - 15 Note
 - 16 The present invention
 - 17 Out of the range of the present invention

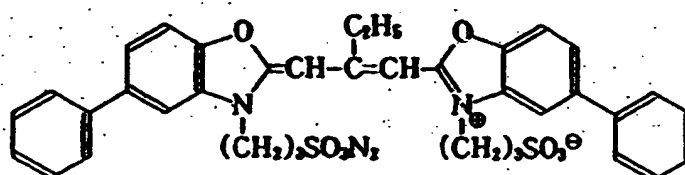
As can be seen from Table 1, although the samples prepared out of the range of the present invention show similar results as the samples of the present invention on the same day,

their properties deteriorate significantly in the two-day deterioration test. On the other hand, the properties of the samples of the present invention are still sufficient for practical application.

Application Example 2

A heat-developable photosensitive material was prepared in the same way as described in Application Example 1 except that 5×10^{-3} mol of the compound shown below was added as the photosensitive coloring material in the composition of Application Example 1. The same test was repeated as described in Application Example 1.

(Photosensitive coloring material)



No.	添 加 剤 ⁽⁹⁾	添加量 ⁽¹⁰⁾ 即 日 ⁽¹¹⁾				40% 80% 2日 ⁽¹⁴⁾			備 考 ⁽¹⁵⁾
		g	比感度 ⁽¹²⁾	カブリ ⁽¹³⁾	D ₉₀	比感度 ⁽¹²⁾	カブリ ⁽¹³⁾	D ₉₀	
①	ブタンテトロール	1.0	100 ⁽¹²⁾	0.10 ⁽¹³⁾	1.25	80 ⁽¹²⁾	0.15 ⁽¹³⁾	1.15	本発明 ⁽¹⁶⁾
②	ペンタンペントール	#	98	0.09	1.31	85	0.16	1.18	
③	ペンタエリスリトール	#	100	0.09	1.20	90	0.13	1.10	
④	ヘキサンヘキソール	#	102	0.12	1.10	85	0.18	1.05	
⑤	アセトアミド	#	102	0.11	1.28	30	0.25	0.73	本発明 ⁽¹⁷⁾ 外
⑥	1,3-ジメチル尿素	#	105	0.12	1.20	29	0.26	0.70	
⑦	マロン酸	#	79	0.05	0.46	—	0.35	0.40	
⑧	ジグリコール酸	#	75	0.04	0.50	—	0.31	0.33	

- Key:
- 1 Butanetetrol
 - 2 Pentanepentol
 - 3 Pentaerythritol
 - 4 Hexanehexol
 - 5 Acetamide
 - 6 1,3-dimethylurea
 - 7 Malonic acid
 - 8 Diglycolate

- 9 Additive
- 10 Amount added, g
- 11 The same day
- 12 Specific sensitivity
- 13 Fog
- 14 40°C 80% RH 2 days
- 15 Note
- 16 The present invention
- 17 Out of the range of the present invention

The results are similar to those of Application Example 1 above. The properties of the samples of the present invention are very good.

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